HIGH COPPER LOW ALLOY STEEL SHEET

BACKGROUND AND SUMMARY OF THE INVENTION

Previously high copper low-alloy steel sheet was known and was known to provide corrosion resistance; however, such low alloy steel containing about 0.50% or more of copper frequently exhibited "hot shortness" during hot working, so that cracks or extremely roughened surfaces, sometimes referred to as "checking," may develop during hot deformation. *See*, *The Making, Shaping and Treating of Steel* (9th edition) at page 1154. Hot shortness occurs by copper separating during surface oxidation from the oxidizing layer to a layer adjacent the surface of the sheet produced resulting in a commercially unacceptable steel. The occurrence of these undesirable surface conditions could be minimized by careful control of oxidation during heating and taking care not to overheat during hot working. Also, the addition of nickel in an amount equal to at least one-half the copper content has been known to be very beneficial to the surface quality of steels containing copper. However, these procedures and alloying additions were expensive and caused the resulting corrosion resistant steels to be expensive. Notably, nickel is an expensive alloy addition and causes the resulting corrosion resistant steel to be expensive.

Copper, in the concentrations used, was known to be the most potent of all common alloying elements in improving atmospheric-corrosion resistance in carbon steels. Copper was known to be especially effective in amounts up to about 0.35% in regular carbon steel. As noted, the steels with about 0.50% or more copper presented the problem of hot shortness. However, these levels of copper were in slabs of the order of 100 mm or more, where the adverse effects of hot shortness could be minimized by the later hot reduction of the strip.

The tolerance for copper is reduced with the reduction in thickness of the slab. For thickness of 50 mm produced in the thin slab caster, it has been found that the copper levels should be about 0.20% or below by weight of copper, to avoid the deleterious effects of hot shortness in the sheet. Indeed, it has been found that the levels of copper typically need to be maintained below 0.10% to avoid the inhibiting impact of hot shortness on the sheet made from the slab. Figures 1 and 2 show the deleterious effects of hot shortness in the surface a slab of 50 mm in thickness

made by a thin slab caster. This was with a steel composition with medium carbon and both copper and nickel additions, namely, 0.18% carbon, 0.53% manganese, 0.009% phosphorus, 0.008% sulfur, 0.025% silicon, 0.23% copper, 0.21% nickel, 0.01% tin and 0.06% chromium. Note that as shown in Figures 1 and 2, even with nickel additions about the same as copper additions hot shortness was experienced.

The problem of hot shortness also increased the costs in making low alloy steel using electric arc furnaces to form the molten steel. Approximately 75% of the cost of making steel by electric arc furnace is the cost of the scrap used as the starting material for charging the electric arc furnace. Steel scrap has been traditionally separated by copper content to less than 0.15% by weight copper, greater than or equal to 0.15% to up to 0.5% by weight copper, and above 0.5% by weight. Scrap with copper content above 0.5% copper was mixed with scrap with low copper levels to make an acceptable scrap, which also added to the cost of the scrap commercially available. In any event, the scrap which was low copper below 0.15% by weight is the highest cost scrap, with the other two grades of scrap being of less cost. In making steel sheet by traditional commercial processes, such as by continuous thick slab or thin slab casting, only scrap with less than 0.15% copper is generally useful in electric arc furnaces. This adds considerably to the cost of the steel sheet produced. Scrap grades with copper content up to 0.5% were useful in electric arc furnaces servicing bar mills, or at considerable expenses, by mixing with scrap of lower copper content to reduce the overall copper content of the scrap.

Applicant has found that high copper low alloy steel sheet of 10 mm in thickness and less can be produced without the addition of substantial nickel alloy by solidification and cooling in a non-oxidizing atmosphere to less than 1080 °C, i.e., below the solidification temperature of copper. In this way, hot shortness is reduced by inhibiting oxidation of the sheet surface. By low alloy steel is meant a steel having between 0.02 % and 0.3% carbon, between 0.10% and 1.5% manganese, between 0.01% and 0.5% silicon, less than 0.04% sulfur, greater than 0.01 % and less than or equal to 0.15% phosphorus, less than 0.05% aluminum, at least 0.20% copper, less than 0.03 % tin,and less than 0.10 % nickel. The copper content of the high copper low alloy steel may be between 0.20 % and 2.0 %. A non-oxidizing atmosphere is an atmosphere typically of an inert gas such as nitrogen or argon, or a mixture thereof, that contains less than about 5% oxygen by weight.

The high copper low alloy steel may also have a corrosion index (I) of at least 6.0 in accordance with ASTM G101-01 where:

$$I = 26.01\ (\%\ Cu) + 3.88\ (\%\ Ni) + 1.20\ (\%\ Cr) + 1.49\ (\%\ Si) + 17.28\ (\%\ P) - 7.29\ (\%\ Cu)(\%\ Ni) - 9.10\ (\%\ Ni)(\%\ P) - 33.39\ (\%\ Cu).$$

The high copper low alloy steel sheet may be made by the steps comprising:

(a) preparing a molten melt producing an as-cast low alloy steel comprising

(i) by weight, between 0.02 % and 0.3% carbon, between 0.10% and 1.5% manganese, between 0.01% and 0.5% silicon, less than 0.04% sulfur, greater than 0.01 % and less than or equal to 0.15 % phosphorus, less than 0.05% aluminum, more than 0.20% copper, less than 0.03 % tin, and less than 0.10% nickel;

(ii) the remainder iron and impurities resulting from melting;

(b) solidifying and cooling the molten melt into a sheet less than 10 mm in thickness in a non-oxidizing atmosphere to below 1080 °C.

The high copper low alloy steel sheet may also be made by the steps comprising:

(a) preparing a molten melt producing an as-cast low alloy steel comprising

(i) by weight percent, between 0.02% and 0.3% carbon, between 0.10% and 1.5% manganese, between 0.01% and 0.5% silicon, between 0.002% and 0.04% sulfur, greater than 0.01 % and less than or equal to 0.15 % phosphorus, less than 0.05% aluminum, more than 0.20% copper, less than 0.03 % tin, and less than 0.05% nickel;

(ii) the remainder iron and impurities resulting from melting;

(b) forming the melt into a casting pool supported on casting surfaces of a pair of cooled casting rolls having a nip therebetween;

(c) counter rotating the casting rolls to form a thin cast sheet or strip of less than 10 millimeters in thickness extending downwardly from the nip; and

(d) cooling the cast strip to below 1080 °C in a non-oxidizing atmosphere.

The thickness of the high copper low alloy steel sheet (or strip)produced may be less than 5 mm in thickness or less than 2 mm in thickness. The copper content of the high copper low alloy steel may be between 0.20 % and 2.0 %. Again, the high copper low alloy steel may also have a corrosion index of at least 6.0 in accordance with ASTM G101-01 where:

$$I = 26.01\ (\%\ Cu) + 3.88\ (\%\ Ni) + 1.20\ (\%\ Cr) + 1.49\ (\%\ Si) + 17.28\ (\%\ P) - 7.29\ (\%\ Cu)(\%\ Ni) - 9.10\ (\%\ Ni)(\%\ P) - 33.39\ (\%\ Cu).$$

Also disclosed is a method for making a high copper low alloy steel of less than 10 mm in thickness. A twin roll caster may be used in making the high copper low alloy steel by the disclosed method as described in more detail below. Again, the high copper low alloy steel strip may be less than 5 mm in thickness or less than 2 mm in thickness.

Brief Description of the Drawings

In order that the invention may be more fully explained, illustrative results of experimental work carried out to date will be described with reference to the accompanying drawings in which:

Figures 1 and 2 are micrographs illustrating hot shortness experienced in the prior art with corrosion resistant low alloy steel made by thin slab casting;

Figure 3 is a diagrammatic side elevation view of an illustrative twin roll strip caster;

Figure 4 is an enlarged sectional view of a portion of the illustrative caster of Figure 3;

Figure 5 is a graph showing the benefits of the high copper low alloy steel of the present invention compared to prior low alloy steel with copper additions;

Figures 6 and 7 are micrographs showing the surface of high copper low alloy steel sheet of 1.7 mm in thickness made by thin strip casting, showing the inhibiting of hot shortness.

Detailed Description of the Drawings

Figures 3 and 4 illustrate a twin roll continuous strip caster which has been operated in making high copper low alloy steel strip in accordance with the present invention. The following description of the described embodiments is in the context of continuous casting steel strip using a twin roll caster. The present invention is not limited, however, to the use of twin roll casters and extends to other types of continuous strip casters and other ways of making steel sheet.

Figure 3 shows successive parts of an illustrative production line whereby steel sheet (or strip) can be produced in accordance with a twin roll caster. Figures 3 and 4 illustrate a twin roll caster denoted generally as 11 which produces a cast steel strip 12 that passes in a transit path 10 across a guide table 13 to a pinch roll stand 14 comprising pinch rolls 14A. Immediately after exiting the pinch roll stand 14, the strip optionally may be passed into a hot rolling mill 16 comprising a pair of reduction rolls 16A and backing rolls 16B by which it is hot rolled to reduce its thickness. In either event, the rolled strip passes onto a run-out table 17 on which it may be cooled by convection by contact with water supplied via water jets 18 (or other suitable means) and by radiation. In any event, the rolled strip may then pass through a pinch roll stand 20 comprising a pair of pinch rolls 20A and thence to a coiler 19. Final cooling (if necessary) of the strip takes place on cooling of the coil after coiling.

As shown in Figure 4, twin roll caster 11 comprises a main machine frame 21 which supports a pair of horizontally positioned casting rolls 22 each having casting surfaces 22A, assembled side-by-side with a nip 27 between them. Molten metal may be supplied during a casting operation from a ladle (not shown) to a tundish 23, through a refractory shroud 24 to a distributor 25, and thence through a metal delivery nozzle 26 generally above the nip 27 between the casting rolls 22. Molten metal thus delivered to the nip 27 forms a casting pool 30 above the nip 27 supported on the casting roll surfaces 22A. This casting pool is confined at the ends of the rolls typically by a pair of side closure dams or plates 28, which may be positioned adjacent the ends of the rolls by a pair of thrusters (not shown) comprising hydraulic cylinder units (or other suitable means) connected to the side plate holders. The upper surface of casting pool 30 (generally referred to as the "meniscus" level) may rise above the lower end of the delivery nozzle 26 so that the

lower end of the delivery nozzle is immersed within this casting pool.

Casting rolls 22 are internally water cooled so that shells of steel solidify on the moving casting surfaces 22A of the rolls 22 during rotation of the rolls. The shells are then brought together at the nip 27 between the casting rolls to produce the solidified strip 12, which is delivered downwardly from the nip.

As illustrated, frame 21 supports a casting roll carriage which is horizontally movable between an assembly station and a casting station. Casting rolls 22 are counter-rotated through drive shafts (not shown) driven by an electric motor and transmission. Rolls 22 have copper peripheral walls formed with a series of longitudinally extending and circumferentially spaced water cooling passages supplied with cooling water. The rolls may typically be about 500 mm in diameter and generally up to about 2000 mm long, in order to produce strip product of about 2000 mm wide.

Tundish 25 is of conventional construction. It is formed as a dish made of a refractory material such as for example magnesium oxide (MgO). One side of the tundish receives molten metal from the ladle and is provided with an overflow spout 24 and an emergency plug 25.

Delivery nozzle 26 is formed as an elongate body made of a refractory material such as for example alumina graphite. Its lower part is tapered so as to converge inwardly and downwardly above the nip between casting rolls 22. Nozzle 26 may have a series of horizontally spaced generally vertically extending flow passages to produce a suitably low velocity discharge of molten metal throughout the width of the casting rolls 22 and to deliver the molten metal onto the roll surfaces 22A of the rolls 22 where initial solidification occurs. Alternatively, the nozzle 26 may have a single continuous slot outlet to deliver a low velocity curtain of molten metal directly above the nip between the rolls and/or the nozzle may be immersed in the molten metal pool 30.

The casting pool 30 is confined at the ends of the rolls by a pair of side closure plates 28 which are adjacent to and held against stepped ends of the rolls 22 when the roll carriage is at the casting station. Side closure plates 28 are illustratively made of a strong refractory material, for example boron nitride, and have scalloped side edges to match the curvature of the stepped ends of the rolls 22. The side plates 28 can be mounted in plate holders which are movable at the

casting station by actuation of a pair of hydraulic cylinder units (or other suitable means) to bring the side plates into engagement with the stepped ends of the casting rolls 22 to form end closures for the casting pool 30 of metal supported on the casting roll surfaces 22A during a casting operation.

The twin roll caster may be of the kind illustrated and described in some detail in, for example, United States Patent Nos. 5,184,668; 5,277,243; 5,488,988; and/or 5,934,359; U.S. Pat. Application No. 10/436,336; and International Patent Application PCT/AU93/00593, the disclosures of which are incorporated herein by reference. Reference may be made to those patents for appropriate constructional details but such details form no part of the present invention.

To illustrate, high copper low alloy steel sheet was made by twin roll caster into thin cast steel strip of 1.7 mm in thickness. The steel strip had the following chemical composition: 0.048% carbon, 0.636% manganese, 0.117% phosphorus, 0.005% sulfur, 0.252% silicon, 0.261% copper, 0.034% nickel, 0.027% chromium, 0.015% molybdenum, 0.006% tin, 0.001% aluminium, 0.001% titanium, 0.001% zinc, and 0.0072% nitrogen. The steel was also tested and not found to have any measurable amounts of vanadium, lead, calcium or boron. This steel was designated heat #232613 (trial #1), and was made into four coils (i.e., numbers 1,2,3 and 4) which were tested.

A second high copper low-alloy steel sheet was made by twin-roll caster into thin cast strip of 1.7 mm in thickness. The steel strip had the following chemical composition: 0.049% carbon, 0.554% manganese, 0.043% phosphorus, 0.009% sulfur, 0.227% silicon, 0.417% copper, 0.030% nickel, 0l.067% chromium, 0.011% molybdenum, 0.005% tin, 0.001% aluminium, 0.001% lead, 0.001% titanium, 0.001% zinc and 0.0065% nitrogen. The composition was also tested for vanadium, niobium, calcium and boron and none were measured. This steel was designated heat #137162 (trial #2), and was made into four coils (i.e., numbers 1,2,3 and 5) which were tested. There was not a roll #4 tested, because it was a pup.

The coils from Trials 1 and 2 were tested and the results are shown in Table 1 below.

Heat # -Coil #	Thickness (mm)	Yield (psi)	Tensile Strength (psi)	Total Elongation (percent)
232613-01	1.7	48,800	74,600	22.2
232613-02	1.7	43,500	76,900	21.2
232613-03	1.7	46,000	72,700	22.2
232613-04	1.7	47,200	76,400	21.7
137162-01	1.7	48,100	67,500	23.2
137162-02	1.7	52,800	71,800	18.2
137162-03	1.7	57,000	73,200	16.2
137162-05	1.7	55,600	73,400	19.7

These data compare well for initial trials with ASTM 606 which specifies a minimum yield of 50,000 psi, a minimum tensile strength of 70,000 psi and a minimum elongation of 22 %. The elongation property of the steel strip in these trials evidences the reduction, if not elimination, of hot shortness since hot shortness typically results in a total elongation in prior steel strip of below 10 %.

Figure 5 shows the dramatic improvement in inhibiting hot shortness with the high copper low alloy steel sheet of the present invention. The solid line illustrates the tolerance of prior art sheet to hot shortness as a function of percent copper from available data. The dotted line is an extension of the solid line showing the projected levels of copper that can be tolerated without hot shortness in sheet below 10 mm in thickness As can be seen from Figure 5, those copper levels are below 0.15 %. By contrast, the levels of copper that can be tolerated without substantial hot shortness in the high copper low alloy steel sheet of the present invention under 10 mm in thickness is more than 0.2%, and 0.4% and higher, with a cast strip of 1.7 mm thickness. Indeed, high copper low alloy steel as high as 1.5% copper has been cast without hot shortness at a thickness of 1.9 mm.

Figures 6 and 7 are micrographs of the surfaces of the high copper low alloy sheet or strip showing an absence of hot shortness. The benefits in inhibiting hot shortness are most evident by comparing Figures 6 and 7 with Figures 1 and 2 above. The high copper low alloy steel also may have a the corrosion index (I) of at least 6.0 where:

$$I = 26.01\,(\%\,Cu) + 3.88\,(\%\,Ni) + 1.20\,(\%\,Cr) + 1.49\,(\%\,Si) + 17.28\,(\%\,P) - 7.29\,(\%\,Cu)(\%\,Ni) - 9.10\,(\%\,Ni)(\%\,P) - 33.39\,(\%\,Cu).$$

Although the invention has been described in detail with reference to certain embodiments, it should be understood that the invention is not limited to the disclosed embodiments. Rather, the present invention covers variations, modifications and equivalent structures that exist within the scope and spirit of the invention and such are desired to be protected.